

Notes on the origin of Bitumens, together with experiments upon the formation of Asphaltum; by S. F. Peckham. Communicated by Prof. J. D. Whitney, Chief of the Geological Survey of California, for the Proceedings of the American Philosophical Society. Sep. 18, 1868.

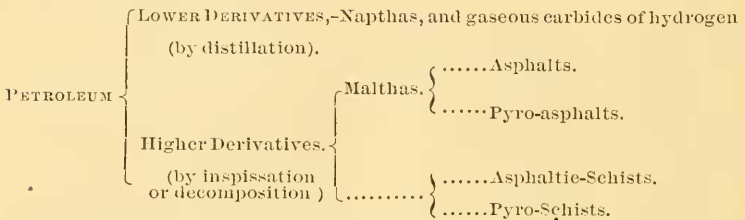
The lack of clear definitions of the specific differences existing between the different varieties of bitumen, or perhaps more strictly speaking, the lack of a uniform and exact nomenclature by which to designate those differences, has led to much confusion in description, and has rendered a comparison of the notes of different observers a task of much difficulty. It is for the purpose of suggesting a more exact nomenclature, as well as to point out the conformity or nonconformity, of the results of my own observations with existing theories, that the following notes are offered.

In all the more extended treatises upon chemistry and mineralogy, definitions are given in more or less detail of naphtha, petroleum, maltha and asphaltum, as varieties of bitumen. The generic relation of the different forms of bitumen and the difference between asphalt and the allied minerals guayaquillite, idrialine, etc.; also the marked differences existing between true solid bitumens and pyrobitumens, or substances yielding bitumen upon application of heat, has been very clearly pointed out by Dr. T. S. Hunt upon several occasions.* He makes fusibility, and solubility in bi-sulphide of carbon a distinguishing test of all true bitumens, and further shows that substances otherwise resembling bitumens which are not soluble in this menstruum are not coals but derivatives of bitumen.

It appears to me desirable that the generic term "Bitumen" should be so employed as to include *all* liquid or solid mineral hydrocarbons soluble in bi-sulphide of carbon, and minerals from which they may be derived which are not true coals; coals from which they may be derived being termed bituminous. Regarding therefore petroleum as the normal form of bitumen, the

* Chem. News, VI. 5, Am. Journal of Sci. and Arts, (2) XXXV. 157.

other varieties derived from it will be found susceptible of the following classification.



The exceptional forms before mentioned, do not perhaps admit of any classification in relation to petroleum, having been formed probably under peculiar circumstances, which were local in their action.

I shall assume, without asserting it to be a fact, that petroleum is the normal or primary product of the decomposition of marine animal or vegetable organisms, chiefly the former, and that nearly all other varieties of bitumen are products of a subsequent decomposition of petroleum, differing both in kind and degree.

Various opinions have been expressed concerning the origin of petroleum. Until quite recently, all of these theories were based upon the assumption that it has been derived from vegetable or animal organisms. It has been supposed to be the product of the decomposition of woody fibre by which more of the carbon and less of the hydrogen has been evolved than by the decomposition which has produced coal. Again, it has been supposed to be the product of the natural distillation of pyrobituminous shales and coals. M. Lesquereux attributes its origin to the partial decomposition of low forms of marine vegetation. Yet, again M. Berthelot has advanced the theory that by complex chemical changes at present taking place in the interior of the earth, petroleum is being continually set free. The following extract translated from his paper, will serve to give an idea of his views upon this subject.

“ If in accordance with an hypothesis recently announced by M. Daubré, it be admitted that the terrestrial mass contains free alkali metals in its interior, this hypothesis alone, together with experiments that I have lately published, furnishes almost of necessity a method of explaining the formation of carbides of hydrogen. According to my experiments, when carbonic acid,

which everywhere infiltrates the terrestrial crust comes, in contact with the alkali metals at a high temperature, acetylides are formed. These same acetylides also result from contact of the earthy carbonates with the alkali metals even below a dull red heat.

“Now the alkaline acetylides thus produced could be subjected to the action of vapor of water; free acetylene would result, if the products were removed immediately from the influence of heat and of hydrogen (produced at the same time by the reaction of water upon the free metals) and the other bodies which are found present. But in consequence of the different conditions the acetylene would not exist, as has been proved by my recent experiments.

“In its place we obtain either the products of its condensation, which approach the bitumens and tars, or the products of the reaction of hydrogen upon those bodies already condensed. That is to say, more hydrogenated carbides. For example, hydrogen reacting upon the acetylene, engenders ethylene and hydride of ethylene. A new reaction of the hydrogen either upon the polymeres of acetylene or upon those of ethylene would engender formenic carbides, the same as those which constitute American petroleum. An almost unlimited diversity in the reaction is here possible, according to the temperature and the bodies present.

“We can thus imagine the production by a purely mineral method, of all the natural carbides. The intervention of heat, of water and the alkali metals, together with the tendency of the carbides to unite with each other to form matters more condensed, are sufficient to account for the formation of these curious compounds. Their formation could thus be effected in a continuous manner, because the reactions which give birth to them are continually renewed. * * *

“This hypothesis is susceptible of further development, but I prefer to dwell within the limits authorized by my experiments without wishing to announce other than geological possibilities.”*

I am convinced that the remains of animal life have contributed much more largely to the formation of petroleum than has been generally supposed, and further that the different varieties

* *Annales de Chemic. et de Physique*, Dec., 1866.

of petroleum are largely due to the varied forms of animal life existing during the different geological epochs to which the rocks belong, from which the oil primarily issues. This latter idea was suggested by a remark of Dr. T. S. Hunt when he says: "their presence" (that is, the petroleums of Pennsylvania and Canada) "in the lower palæozoic rocks which contain no traces of land plants, shows that they have not in all cases been derived from terrestrial vegetation but may have been formed from marine plants or animals; the latter is not surprising when we consider that a considerable portion of the tissues of the lower marine animals is destitute of nitrogen and very similar in chemical constitution to the woody fibre of plants.*"

This opinion is further strengthened and confirmed when we find in rocks of tertiary age, in which fossil remains of the higher marine animals are found in abundance, a petroleum comparatively rich in nitrogen, of unstable constitution and undergoing decomposition in a manner similar to putrefaction. Such is the character of the petroleum issuing from the Miocene of the coast ranges of Southern California, and from such meagre accounts as are accessible, I infer that such are the characteristics of the petroleum of the Baku region on the shores of the Caspian Sea, issuing from rocks which I am assured by the Baron Koschkull are also of Miocene age.

Let us examine these different theories. Bischof has shown very clearly and with abundant illustrations, the manner in which the decompositions may be effected which produce the different kinds of coals and bitumens from wood.† These illustrations have been abridged and arranged in tabular form by Dr. Hunt, in a paper published in the sixth volume of the *Chemical News*.‡ The reactions necessary to produce petroleum instead of coal have been further traced by him in the article before quoted from the *American Journal*.§ The theoretical possibility of such a decomposition requires no further proof, but it should be observed that these theories are based upon the results of ultimate not proximate analysis.

If it be granted that a theoretical compound may be obtained from cellulose having an equal number of equivalents of carbon and hydrogen, the general formula for petroleum, the fact still remains that petroleum has never been observed under such

* *Chem. News*, VI. 5.

† *Chem. News*, VI. 35.

‡ *Chem. and Phys. Geology*, I. 274.

§ *Am. Jour. Sci. and Arts*, (2) XXXV. 158.

circumstances as to leave no possibility of a doubt that it was derived from wood. The observations of Mr. J. P. Lesley are the most conclusive of any that I have met, yet, it appears to me the facts as observed by him, may be accounted for upon an hypothesis more in harmony with those connected with the occurrence of mineral oils in other localities.* Several instances are cited by Bischof, in illustration of the fact that wood has changed to lignite during the historic period.† The discovery of the piles driven in the Thames by the ancient Britons, and of timber in long abandoned mines, both found in a carbonized condition, will serve as examples. Still more recent discoveries were made at Port Hudson, La., where wood bearing the marks of the axe was found in a sedimentary deposit of the Mississippi river in a carbonized or as the writer expresses it, bituminized condition.‡ It is therefore to be inferred that the formation of petroleum from woody fibre presupposes a peculiar decomposition, under conditions so extraordinary as not to exist at present; conditions too that though possible during former geological epochs were then by no means universal, as is proved by the fact that petroleum and coal alike occur in almost every formation from the primary to the tertiary, and often in close proximity to each other. The formation in Southern California in which petroleum and other forms of bitumen occur in vast quantities, contains lignitic remains at rare intervals, proving that the conditions essential to the formation of lignite and petroleum were present at the same time.

Again, coal is a compound body, while petroleum is a compound of compounds—a mixture of many substances of definite constitution. Substances identical with those existing in petroleum may be obtained from coal, but it is only upon the decomposition of the coal that they are obtained, while they exist in the petroleum already formed. These substances are also formed by the destructive distillation of wood with exclusion of oxygen, but they do not exist in the wood already formed, and are only formed artificially, by processes which are not analogous to any which we have a right to suppose have ever been active in *nature*. Animal matter may be subjected to such

* Pro. Am. Phil. Soc. X. 33 and 187. † Chem. and Phys. Geology, I. 294.

‡ Am. Jour. (1) XXXV. 345—XXXVI. 118. From the description it appears that the remains were lignitic rather than bituminous.

researches of Profs. Warren and Storer. They saponified Menhaden Oil with lime and then distilled the lime soap.* Upon rectifying the lighter portions of the crude distillate and subjecting it to the process of fractionation invented by Prof. Warren, they obtained the identical hydrocarbons found by them in Pennsylvania petroleum. Taken as a whole the distillate resembled more nearly Rangoon petroleum, which has been analyzed by the same gentleman.

The facts just mentioned when viewed by themselves, suggest the theory that petroleum is the product of the distillation of pyrobituminous minerals by natural processes. Excepting in the case of some of the lightest varieties, more properly termed naphthas, I do not consider that there is any further evidence to support such an hypothesis. The discovery of strata saturated with petroleum or the products of its decomposition, while those above and below do not contain a trace of it, is sufficient in itself to refute such an opinion.

The opinions entertained by M. Lesquereux when applied to petroleums issuing from palæozoic rocks, are perhaps as little open to objection as any theory of which I have spoken; but as a formula applicable to all conditions under which petroleum occurs, they cannot be maintained. Even when confined to the application which he has made of them, I think they claim too exclusively a vegetable origin. It would be equally open to objection to claim that those oils were without exception of animal origin. The differences between the animal and vegetable life of a deep sea fauna, both in functional and elementary organization, are too slight to admit of any nice theoretical distinctions being drawn respecting the products of their decomposition. A mass of polypi undergoing decomposition upon a beach would doubtless saturate the sand with carbonaceous matter as readily as an equal bulk of algæ. If petroleum were invariably derived from marine algæ, we should expect to find it identical in composition wherever found, as the conditions favorable to their growth and their composition are in all cases too nearly identical to admit of any marked variation in the products of their decomposition. We should not therefore expect to find in one formation a very stable substance, and in another treatment as to yield similar results, as has been shown by the

* Mem. Am. Acad. N. S. IX. 177.

one equally unstable, yet both derived from a source which has varied but slightly, if at all, through all geological epochs.

The theory of M. Berthelot appears to me to derive less support from observed facts than any which has been proposed. It was doubtless formed with reference to the petroleum of Pennsylvania, which are among the purest mineral hydrocarbons of any found in large quantities. The very small proportion of nitrogen existing in these oils, might perhaps be accounted for as an accidental constituent of the limestone, or as being mechanically mingled with the carbonic acid or watery vapor. Neither supposition is at all probable, since free nitrogen possesses such slight affinities. It adds nothing to its support to admit that the alkali metals do exist in the interior of the earth, in the free state. The very great difference observed between the varieties of petroleum, cannot be satisfactorily explained upon any hypothesis, that regards them as the results of the same process acting upon like materials; neither should it be expected that a process yielding an almost "unlimited diversity" of products under slightly varying circumstances, would furnish a uniform result over a very wide area. Samples of Pennsylvania petroleum of the same density, when gathered from widely separated localities, furnish identical results upon analysis; so too do California petroleum, though gathered from localities fifty miles apart, and yet the two varieties of oil are exceedingly unlike. "It is moreover altogether erroneous, to attempt to explain the causes of geological facts, by the aid of supposed analogies with the complex apparatus of physical cabinets, whose existence in nature could scarcely be conceived by the boldest and most unrestrained imagination."*

Too much has been assumed concerning the constitution of all petroleum from the researches of the few investigators who have studied Pennsylvania petroleum. Because Messrs. Warren and Storer discovered that the same proximate principles exist in that portion of Pennsylvania and Rangoon petroleum boiling at or below 200° C., yet not in the same relative proportion, and not without admixture of different substances, it must not be taken for granted that all petroleum contain those principles. Very little is at present known concerning the more dense portions of Pennsylvania petroleum having boiling points

* Bischof. Chem. and Phys. Geology, I. 243.

above 200° C., amounting to about thirty per cent. by measure. When this dense portion amounts in other petroleums to about seventy per cent., even should the lighter portions contain the same principles, the question of similarity between the two oils requires a comparison of the heavier quite as much as the lighter portions.

The small proportion of nitrogen found in the petroleums of the palæozoic rocks of Pennsylvania and Canada, might be derived from any source to which the origin of petroleum has yet been ascribed; but when we pass up from those early formations through the secondary rocks to the middle tertiary, to a deposit rich in remains of the higher marine animals, in which cetacean bones are as frequently met as any other fossil, and find an oil comparatively rich in nitrogen, we are forced to admit that the conditions of such theories are less in accordance with facts. The decomposition of carbonic acid and water by alkali metals would scarcely be expected to produce an hydrocarbon of very unstable character, containing so large a proportion of nitrogen as to render its decomposition analogous to putrefaction. Nor should we expect such results from the partial decomposition of vegetable matter, either of terrestrial or marine origin. The small proportion of nitrogenous matter in the woody structure of forest trees, and the still smaller proportion in marine vegetation would fail to furnish the requisite amount, but in the partial decomposition of the remains of highly organized animal tissue, we have an abundant source of nitrogen.

Dr. Hunt has shown the possible derivation of compounds having an equal number of equivalents of carbon and hydrogen, similar to or identical with petroleum, from the decomposition of animal tissue. He discusses this possibility however, only with reference to the bitumens "met with in the lower Silurian and Devonian limestones of marine origin."*

It is not difficult to propose a theoretical decomposition of many of the proximate principles of animal origin, which would yield a substance having an equal number of equivalents of carbon and hydrogen. Thus, if six equivalents of carbonic acid be removed from one equivalent of stearic acid, an equal number of equivalents of carbon and hydrogen remain. One equivalent each of stearate and oleate of glycerine, when deprived of sixteen equivalents of carbonic acid and four of water, yield two

* *Am Jour. Sci. and Arts*, (2) XXX. 162.

hundred and twenty-four equivalents each of carbon and hydrogen.

The protein compounds of which animal tissues are composed contain carbon and hydrogen in nearly equal proportions and largely in excess of either of the other constituents. It would be difficult to devise any method by which they could undergo decomposition, with exclusion of oxygen, without producing an hydrocarbon or a variety of such bodies, and it is highly probable that they would contain nitrogen. When a mass of animal matter, consisting not only of the muscular tissue but of all the non-nitrogenous substances entering into animal organisms, was thus subjected to decomposition submerged in water, the product could not fail to be a nitro-hydrocarbon, which upon exposure to atmospheric oxygen would undergo a second decomposition into a greater or less number of the following named products, carbon, hydrocarbons, ammonia or free nitrogen, carbonic acid and water. The petroleum of Southern California, issuing primarily from Mioocene shales, are of precisely this unstable character.

Although we have not that direct evidence of the formation of *all* petroleum from animal remains, that the carbonization of wood during the historic period and its cellular structure furnishes of the derivation of coal, we are not without positive proof that such a decomposition is possible through the agency of natural causes. Solid bitumen has been repeatedly found filling the cavities in the Lias of England, once filled with the gigantic marine lizards of that formation. "In some cases," says Dr. Hunt, "petroleum is found filling cavities in silurian limestones, as at Rivière de la Rose (Montmorenci) where it flows in drops from a fossil coral of the birds-eye limestone; and at Pakenham where it fills the cavities of the large orthoceratites in the Trenton.*" In one locality in California, a shaft was sunk upon an oil spring in the belt of oil shales. A reliable witness informed me that the excavation passed for several feet through a mass of fossil bones which were saturated with oil. The mass when thrown out retained the cellular structure of bone for several days, but finally crumbled on exposure to the atmosphere.

It may be urged that if petroleum was of animal origin it

* Chem. News, VI. 15. Am. Jour. (2) XXXV. 166. A very large number of similar instances are mentioned by Dr. Hunt and Dr. J. S. Newbury, as occurring in the United States and Canada.

would contain both phosphorous and sulphur. Phosphate of lime is quite freely soluble in water saturated with carbonic acid; and sulphuretted hydrogen is soluble in cold water excepting when it contains a free acid. Bones too are soluble in water containing either carbonic acid or chloride of sodium or ammonium.* Since water almost invariably contains carbonic acid, these products of decomposition would soon be borne away. Sulphates, especially those of the alkalies, when in solution, are decomposed when the water containing them flows through strata impregnated with organic matter, into sulphuretted hydrogen and a carbonate of the oxide present. When sulphuretted hydrogen infiltrates strata containing carbonate of lime, gypsum is formed and sulphur deposited.† Nearly every spring of bitumen in Southern California yields also more or less water, containing organic matter in solution, together with salts of soda, chiefly sulphate, carbonate and chloride. The water is also almost without exception, highly charged with sulphuretted hydrogen, and deposits of sulphur of considerable extent are of frequent occurrence, often accompanied with gypsum in irregular masses. As sulphur is sparingly soluble in petroleum, those of that region all contain it in small proportion. Should the water which accompanies the oil in Pennsylvania, be found to be free from sulphates, especially those of the alkalies, the fact would furnish an explanation of the remarkable freedom of those oils from sulphur. In the few instances in which oil containing sulphur has been found in cavities of fossils hermetically sealed, the sulphur might have been derived from the animal remains from which the oil originated.‡

In accordance with the foregoing conclusions, I repeat, let it be assumed that petroleum is the normal or primary product of the decomposition of organic matter, chiefly animal, then the different varieties are found to fall into two groups. The first group forms asphaltum by inspissation, if at all; it contains paraffine, and the products of the distillation of all the forms of bitumen derived from it, yield paraffine. This group I shall designate the class *A*, and it may be represented by the petroleum of the Oil Creek region, Pennsylvania. The second group forms

* Bischof Chem. and Phys. Geology. II. 28.

† Ibid. I. 15 and 340.

‡ It would be of interest to know if any instances occur in which the limestone surrounding these cavities has been replaced by gypsum.

asphaltum by decomposition, it does not contain paraffine, neither do the distillates from any of its derivatives; this group I shall call the class *B*, and it may be represented by the petroleum of Southern California. The derived forms of these different classes are designated, asphalts of the class *A*, pyro-asphalts of the class *B*, etc.

The word naphtha is used to designate the most volatile products of the distillation of wood, coal or petroleum. When restricted in its use to this class of substances, it indicates an extremely volatile product of distillation, composed of carbon and hydrogen. The loose manner in which this term has been applied to products of exceedingly unlike character, has led to much confusion in description. I propose in this connection to limit its use to those extremely volatile and slightly colored mineral oils, which are occasionally met with in different localities, and which are evidently the product of a distillation carried on by natural processes.*

Gaseous carbides of hydrogen almost invariably accompany deposits of bitumen of every variety.

Maltha or mineral tar is, as its name implies, more nearly allied to tar in its physical properties than to oil. It is usually described as distinguished from petroleum by its viscosity, but a more marked dissimilarity is found in the manner in which the two are separated from mechanical admixture with either gaseous or liquid impurities. When petroleum is mingled with either water or air, they readily separate, as soon as the mixture is allowed to remain at rest, leaving the petroleum in a state of purity. With the more dense varieties this separation may be assisted by the aid of a gentle heat. Petroleum which has been thus separated from these impurities may be heated to its boiling point, when gentle ebullition ensues. If however an attempt is made to boil petroleum before such separation is complete, the water will subside as the temperature is raised, until at 100° C, the ebullition will become explosive from the escape of intermittent puffs of steam.

Crude maltha which has escaped from a fissure in a rock, or has been pumped from a well accompanied by water, in falling into a tank, entangles air in its descent. Many of the larger bubbles of both air and water readily separate, but the separa-

* See Humbolt's Travels, I. 198; III. 113, Bohn's Ed.

tion will not be complete if the maltha should remain at rest for months. When placed in tanks and moderately heated for a long time the separation is still incomplete. As the temperature is raised the liquid commences to foam, the foam finally occupying many times the bulk of the maltha. A sample of California maltha which I examined, appeared to be a pure black viscous bitumen of uniform consistence. When heated it began to foam perceptibly when the temperature was raised only ten degrees Fahr., and at 100° it foamed so rapidly that retort and worm were soon entirely filled. When heated in an open vessel the foam occupied about twenty times the bulk of the maltha, and the air and water were not expelled until the temperature had reached 230° Fahr.

The surface oils or tars obtained from the so-called surface wells, bored in the superficial detritus at Emmiskillen, were malthas possessing this characteristic of viscosity, and presenting the same obstacles to successful distillation encountered in those from California.

The same causes which produce the lighter varieties of maltha from petroleum, whether it belong to the class *A* or *B*, if their action be continued, will cause the bitumen to become more and more dense, until it attains the consistency of pitch and finally hardens into solid asphaltum. The line of separation between maltha and asphaltum is wholly arbitrary.

Of the solid bituminous minerals which are derived from petroleum, there are four distinct species, viz: asphaltum, pyroasphaltum, asphaltic schists and pyroschists. The first two are pure bitumens, amorphous, with a brilliant conchoidal, sometimes angular, fracture. Asphaltum is soluble in bi-sulphide of carbon, pyroasphaltum is insoluble, but both yield a distillate soluble in that menstruum. Asphaltic schists and pyroschists are produced either by the saturation of pervious strata with petroleum, or by the admixture of organic and earthy matter during the deposition of sedimentary strata, and their subsequent transformation into asphaltum. Under these two species may be included as varieties, all those bituminous minerals in which the earthy matter preponderates, whether it be sand, slate or limestone. They may be distinguished from each other by the same tests which serve to discriminate between asphalts and pyroasphalts. The pyroasphalts and schists are derived from the

asphaltic minerals by a change which renders them less soluble and fusible, and more nearly resembling coals.

The derivation of solid forms of bitumen from the class *A*, presupposes the possibility of forming asphaltum by the *inspissation* of petroleum. There are many small deposits filling cavities in rocks, both of asphalts and pyroasphalts, mentioned by Dr. Hunt and others, which *may* have been formed in this manner.* I am however extremely doubtful if the veins of so-called inspissated petroleum, of which albertite is an example, are not more probably the product of the distillation of asphaltic or pyroasphaltic schists, at a very low temperature, resulting from their metamorphosis. This view obtains additional force, if the theory be admitted that metamorphic action has taken place through the agency of watery vapor, as the distillation would then have taken place at the lowest temperature, under conditions favorable to the production of the largest quantity of distillate, of the greatest density possible. The enormous quantity of petroleum of ordinary density, which would upon inspissation furnish a solid residue, sufficient to form a deposit equal in extent to that of the albertite, can scarcely be conceived of even when compared with such vast accumulations as those of Pennsylvania and Rangoon.

Enormous deposits of asphaltum have been formed in California by the decomposition of petroleums of the class *B*. Asphaltic schists of the same class are also numerous in that region.

The classification of bitumens which I have adopted, was suggested by the results of many months' study of the formation of asphaltum in California, by natural causes, and by the results of analysis and experiments upon California and Pennsylvania petroleums, made in the laboratory of Brown University.

Throughout the oil-belt of Southern California, every form of bitumen derived from petroleum of the class *B*, is found, with the exception of naphtha, pyroasphalts and pyroschists. Light petroleums of a beautiful green color, pass through every degree of blackness and density to solid asphaltum. None of the natural forms, nor distillates produced from them, contain a trace of paraffine. The green oils upon exposure to atmos-

* Rep. Geo. Sur. of Canada, 1866, pp. 252 and 262; Vanuxem Rep. Geo. Sur. of New York.

pheric action soon become brown or black, but the increase in density is very gradual. These changes are not all produced upon the surface, as many of the springs yield maltha of varying density, and wells bored to a depth of from fifty to four hundred feet, have yielded bitumen which had undergone a greater or less change. A careful study of the different exposures over a very wide area, when taken in connection with the above mentioned facts, convinced me that such changes could not possibly be produced by inspissation, even in the warm climate of Southern California. I soon became equally well satisfied that they were due entirely to the action of atmospheric air, conveyed through the agency of rain water. Wherever the belt of shales from which the oil primarily issues is exposed in a nearly or quite perpendicular bluff, in which the shales are overlaid with impervious strata of sandstone or by several hundred feet of shales, the oil reaches the surface unchanged; but when the outcrop occurs near the base of a gentle slope, or near the summit of the hills, in situations where the oil shales are horizontally exposed to the action of meteoric water over areas of considerable extent, the bitumen exudes of a density increased in proportion to the amount of exposure to which it has been subjected. The subterranean reservoirs of Pennsylvanian petroleum are overlaid by slightly disturbed and inclined strata of impervious sandstones, while the oil shales of California contain few large fissures but innumerable small ones, the fluid being held in them by capillary attraction and between the layers of shale, consequently exposing a very large surface of oil to contact with water, wherever the strata are so exposed as to admit of its infiltration. The strata in that region are very much broken and inclined at very high angles.

I became convinced at a very early date in my study of this subject that the difference in exposure alone, would perhaps account for the difference in the average density of the Pennsylvania and California oils, but the discovery of the fact that the latter did not contain paraffine, and that it was not found in oils distilled from them, led me to question the identity of these oils in chemical constitution.

The researches of Prof. Warren upon volatile hydrocarbons from various sources have shown conclusively, that ultimate analyses of crude petroleums are of little or no assistance in

making comparisons between them. I have not yet been able to devote the length of time required to make a complete separation of the proximate principles contained in the California Oils, but have accomplished enough to strengthen my first impression, that they are unlike those of corresponding density found in Pennsylvania Oils.

Having observed upon several occasions, small pools of California maltha which were literally filled with the larvæ of insects, I was led to believe that those oils contained an unusually large proportion of nitrogen. I therefore embraced the first opportunity offered, to make analyses of several samples and compare the results with that of an analysis of Pennsylvania Oil.*

The samples of California Oil had been gathered about nine months previous, that of Pennsylvania Oil I should think had been gathered about five months.

The results were as follows :

1 Sample	1.140 } 1.070 }	mean 1.105 per cent.
2 "	1.026 } 1.007 }	" 1.0165 "
3 "	1.088 } 1.083 }	" 1.0855 "
4 " Maltha	.545 } .584 }	" .5645 "
Pennsylvania Oil	{ mean of three } { analyses }	.1912 "

The first sample was more dense than the second, but had been least exposed to atmospheric action. These results led me to infer, that the change consisted in the breaking up of unstable nitrogenous compounds, with deposition of uncombined carbon and consequent thickening and blackening of the oil.

One year later, wishing to test apparatus and materials for the further prosecution of this research, I made a trial analysis of the first sample, and was surprised to find that the quantity of nitrogen had diminished by more than one half. The analysis was repeated with the following results :

.493	
.485	
.486	mean .48775 per cent.
.487	

* Mr. Moss, Supt. of an Oil Estate near San Buena Ventura, stated to me that oils fresh from tunnels, when exposed for a few days in a shallow dish, became filled with maggots.

The other samples furnished similar results. A portion of the first sample added to a portion of chemically pure Urea, gave the estimated quantity of nitrogen within a few thousandths of one per cent. A sample of Mecca Oil furnished me by Dr. J. S. Newbury, yielded .230 per cent., and another from the Cumberland Well, W. Va., furnished me by Prof. E. B. Andrews, yielded .054 per cent. The California Oils had been kept during the year in partially filled tin oil cans, closed with a cork. The loss of nitrogen was not accompanied by a corresponding increase in density, but the color had changed from dark brown to black. These results proved the change to be only in very small part due, to the breaking up of nitrogenous compounds.

I then determined to study the action of powerful oxidizing agents upon the two varieties of oil. For this purpose I first attempted to generate ozone by phosphorous, but found it very difficult to manage. I then had recourse to the action of concentrated sulphuric acid upon dry per-manganate of potash, as a source of ozone. With these reagents I was entirely successful. The first per-manganate that I used, contained a portion of undecomposed chlorate, and consequently gave off chlorine as well as ozone. Twenty-five grams each of the California and Pennsylvania Oils were subjected to the action of the mixed gases under identical conditions. The gases passed through the California Oils in small bubbles, each bubble being covered with a film of oil, which rising and adhering to each other filled the vessel, until a sudden collapse made room for more. With the Pennsylvania Oil the bubbles rose to the surface and burst. The quantity of both oils diminished in weight as the action was prolonged from two to fifteen days, but not in proportion to the length of time, as the amount of gases generated were greater for the time during the shorter than the longer period. No change whatever was perceptible in the Pennsylvania Oil excepting an increase in specific gravity. It remained perfectly fluid, retaining its color and partial transparency, and no sediment was deposited from it. With the California Oils on the contrary the action of the gases was extremely energetic. As the first portions passed through the oil and collapsed, minute particles of solid bitumen were left as the residuum of each bubble. As the action was prolonged the specific gravity of the

oil was increased, and solid bitumen in proportionally large amount was precipitated to the bottom of the vessel. After decanting the liquid portion from the solid, the latter was found to be a brittle asphalt, having a brilliant fracture, readily soluble in bi-sulphide of carbon and fusible at the boiling point of water. The minute particles first deposited were insoluble in that menstruum and infusible at the temperature before mentioned.

I next subjected other portions of the same samples to the action of ozone, prepared from pure and dry per-manganate of potash. The action of this gas was less energetic than when it was mixed with chlorine. No solid bitumen was formed insoluble in bi-sulphide of carbon, but in other respects its action upon each of the oils was not to be distinguished from that of the mixed gases. A third series of experiments were made by passing atmospheric air through portions of the same samples. The time was prolonged to fifty days, yet as in the former experiments with chlorine and ozone, the Pennsylvania Oil presented no change, which might not be attributed to very slow evaporation, retaining entirely its peculiarities of color, being changed only in consistence, which became as honey, and losing at least three-fourths of its bulk and weight.* No solid bitumen was deposited from the California Oil in this experiment. It diminished somewhat in bulk and weight, but increased in specific gravity in much greater proportion to its loss, than the Pennsylvania Oil.

An experiment made to ascertain the products of the decomposition, effected by the ozone upon the California Oil, failed to detect water, but exhibited carbonic acid in abundance, undoubtedly accompanied by gaseous carbides of hydrogen, although of the latter supposition I have as yet no positive proof.

It would be useless at present to attempt to form even a speculative explanation of the reactions which take place in the decomposition which forms asphaltum, as nothing is as yet known of the proximate principles which make up California petroleum.

These results of observation and experiment, simple as they may at first appear, are nevertheless the first steps towards a

* May not "Ozocerite" and other semi-transparent and elastic solid bitumens, be formed by the very gradual evaporation of petroleum resembling those of Pennsylvania?

correct and successful study of the dense liquid and the solid forms of bitumen. Ultimate analysis fails to throw any light upon the true character of a solid bitumen. It may detect traces of nitrogen, sulphur or oxygen, but fails to show whether they are essential or accidental elements — whether they belong to asphaltum or whether they are derived from organic impurities, with which every surface asphalt is contaminated. Methods of analysis requiring a high temperature are especially unsatisfactory, because it is impossible to discriminate in the results obtained between products of decomposition and those of composition. By perfecting and extending the application of this process to a large number of liquid bitumens of known constitution, and studying the results of their decomposition, both solid and gaseous, a method which in relation to asphaltum may in one sense be termed synthetic, the answer to this most interesting question of the origin of bitumens, may in some degree at least be removed from the domain of pure speculation to that of positive knowledge.

More extended research may lead to a modification of the views herein expressed. It appears to me not unlikely that petroleums exist intermediate between the classes *A* and *B*, which contain proximate principles found in each of them, and which, while they contain the paraffine series, may be susceptible of experiencing the asphaltic change. It may also appear probable that the more stable class *A* are entirely of vegetable origin, while the class *B* is of animal origin; a third and intermediate class, should it be found to exist, being derived in part from both sources. It is my intention to continue this research, not only in order to obtain more exact results respecting those oils already examined, but to extend its application to other petroleums. My object at present will be accomplished, if I call the attention of those engaged in the study of petroleums, to the consideration of these questions, the importance of which to science and technology, circumstances have strongly impressed upon my own mind.

PROVIDENCE, R. I., *July 28th*, 1868.